Geometries, interaction energies and complexation free energies of 18-crown-6 with neutral molecules

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Although 18-crown-6 is renowned for its binding affinity to various metal and ammonium cations, the nature and strength of its binding with neutral guest molecules is relatively unexplored. Here we report a computational study of the host:guest geometries, interaction energies and Gibbs free energies of formation of 18-crown-6 with 49 neutral guest molecules in the gas phase, using the G4(MP2) composite method. Optimized geometries are in excellent agreement with those observed in crystals, with differences readily attributed to guest:guest interactions in the solid state. Host:guest interaction energies range from -13 to -103 kJ mol⁻¹, and the estimated Gibbs free energies of binding at 298 K correlate with the observation (or not) of the complexes in crystals. The electrostatic, dispersion, polarization and repulsion components of the interaction energy have also been estimated using the recently described CE-B3LYP model energies, providing insight into the binding nature between 18C6 and neutral molecules.

Introduction

Since their discovery in 1967, crown ethers have attracted much attention, in the process providing an important foundation for modern supramolecular chemistry.² They have found extensive applications in cation transportation and separation,³ and recently crown ethers have been used in the design of ferroelectric materials⁴ and responsive organic polymer gels.⁵ Most applications of the crown motifs are based on their ability to offer supramolecular recognition units that can selectively bind to certain cationic species. In this context, many computational studies have been reported on crown ethers, with the majority of them focused on the binding energy and nature of interaction between the crown ether and metal or ammonium cations.⁶ Somewhat surprisingly, the binding of crown ethers with neutral guest molecules has been largely bypassed by current computational and supramolecular chemists. However, the ability to bind neutral molecules is one of the most important properties of crown ethers; 18-crown-6 (18C6), one of the most common crown ethers, is well known for its ability to form stable and ordered complexes with a vast number of neutral molecules possessing structural elements – OH, –CH₃ and –XH₂ (X = N, C) in the solid state.⁷ These range from common solid-state neutral molecules such as malononitrile⁸ and urea⁹ to low vapour pressure solvents such as acetonitrile,¹⁰ and dichloromethane,¹¹ and gases such as

ammonia.¹² The fact that the corresponding crystals formed by these host:guest complexes are stable implies strong binding affinities, and these form the focus of the present study. While the interaction energies between 18C6 and ammonium cations have been shown to range from -200 to -270 kJ mol⁻¹,^{6c} our recent research has shown that in the host:guest complexes formed by 18C6 and sulfonamide analogues the interaction energies between host and guest are typically between -90 and -100 kJ mol⁻¹.¹³ In fact the host:guest binding energies of these sulfonamide-crown motifs have been found to be much stronger than other intermolecular interactions in those crystalline complexes; they are clearly the structure-determining motif.

To the best of our knowledge there are very few computational reports of geometries, interaction energies and free energies of formation between 18C6 and neutral molecules. Early molecular mechanics studies focused on the geometry of the crown and its complexes with urea and formamide,¹⁴ malononitrile, nitromethane, acetonitrile and dimethylsulfone,¹⁵ and malononitrile, nitromethane, acetonitrile and benzene.¹⁶ More recent computational studies have explored the hydrates of 18C6,¹⁷ and gas phase structures of 18C6:phenol have been determined to complement a laser spectroscopic study.¹⁸ Here we report the geometries, interaction energies and free energies of binding in 1:1 supramolecular complexes of 18C6 with 49 common neutral molecules in the gas phase. Benchmark interaction energies are calculated by means of the G4(MP2) composite method¹⁹ and are compared with CE-B3LYP²⁰ model energies from CrystalExplorer,²¹ which partitions the total energy into electrostatic, polarisation, dispersion and exchange-repulsion

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components. This partitioning is used to explore the origin of host:guest binding among various classes of guest molecules. appropriate.

Results and Discussion

Computational Details

Ab initio and density functional theory calculations for gas phase dimers between 18C6 and neutral molecules were carried out using the Gaussian 09²² and Molpro 2012²³ program suites. Geometry optimisation and vibrational frequencies were obtained at the B3LYP-D3BJ/6-31+G(2df,p) level of theory for isolated monomers and dimers. Empirical D3 dispersion corrections²⁴ were included using the Becke-Johnson²⁵ damping potential,²⁶ and all the complexes were verified to be equilibrium structures (i.e., all real frequencies). We cannot guarantee that the structures obtained for 1:1 complexes correspond to the global minimum, but we have explored the potential energy surfaces in reasonable detail, and the structures reported correspond to the lowest energies that we found. Enthalpies (ΔH_{298K}) and Gibbs free energies of complexation at 298 K (ΔG_{298K}) were obtained via standard procedures using the G4(MP2) variant¹⁹ of the Gaussian-4 composite thermochemical protocol,^{19, 27}

CE-B3LYP is an efficient energy estimation procedure designed to obtain accurate model energies for intermolecular interactions in molecular crystals.²⁰ The approach uses electron densities of unperturbed monomers to estimate electrostatic, polarization, and repulsion energies, which are combined with Grimme's D2 dispersion corrections²⁸ to derive a family of energy models by scaling the separate energy components to fit B3LYP-D2/6-31G(d,p) counterpoise-corrected energies for a large number of molecular pairs extracted from molecular crystals. CrystalExplorer²¹ was used to obtain interaction energies with the best performing of these models (CE-B3LYP) from B3LYP/6-31G(d,p) molecular wavefunctions calculated for monomers at the geometries obtained in their respective complexes.

Interaction energy, enthalpy, entropy and Gibbs free energy of host:guest complexation

Table 1. G4(MP2) and CE-B3LYP electronic energies (ΔE), and G4(MP2) enthalpy (ΔH_{298K}), entropy ($T\Delta S_{298K}$) and Gibbs free energy (ΔG_{298K}) for complex formation at 298 K (kJ mol⁻¹). Entries are listed from most positive to most negative ΔG_{298K} .

Guest	ΔE	ΔE	ΔH_{298K}	ΔG_{298K}	$T\Delta S_{298K}$
	G4(MP2)	CE-B3LYP			
CO	-12.5	-17.3	-8.6	30.0	-38.6
CF ₄	-27.3	-34.2	-21.6	19.4	-41.0
Methylcyclopentane	-38.9	-39.9	-32.3	16.2	-48.6
SiH ₄	-34.0	-35.6	-27.0	15.4	-42.5
C ₃ H ₈	-30.1	-29.7	-23.8	11.9	-35.7
Methylcyclobutane	-35.4	-35.9	-29.2	10.8	-39.9
C ₂ H ₆	-24.6	-23.8	-18.9	10.7	-29.6
CH ₄	-17.2	-18.3	-11.5	9.9	-21.4
PH ₃	-33.1	-29.0	-26.9	8.9	-35.7
C ₂ H ₄	-29.2	-25.9	-23.3	8.4	-31.6
CH ₃ COCH ₃	-47.5	-49.5	-40.5	8.4	-48.9
CH ₃ OCH ₃	-38.5	-38.9	-31.7	7.8	-39.5
Methylcyclohexane	-39.2	-39.3	-32.7	7.5	-40.1
NH ₃ ^[a]	-39.6	-48.1	-31.9	5.5	-37.5
CH ₃ CHO	-46.3	-48.1	-38.6	3.1	-41.7
NH ₂ CH ₃	-45.3	-47.5	-37.8	2.4	-40.3
H ₂ S	-39.9	-39.7	-33.2	1.2	-34.4
NH ₂ CH ₂ CH ₃	-49.5	-50.4	-41.9	0.1	-42.0
CO ₂	-49.8	-51.0	-45.3	0.0	-45.2
CH ₃ COOH ^[a]	-52.0	-82.9	-43.9	-0.1	-43.8
Toluene	-46.8	-43.1	-37.7	-0.3	-37.3
C ₂ H ₂	-32.6	-26.7	-28.0	-1.4	-26.6
CCl ₄	-40.1	-26.6	-34.3	-1.4	-32.9
CH ₃ Cl	-46.2	-49.5	-39.2	-1.7	-37.4
CS ₂	-40.6	-21.9	-36.1	-3.0	-33.1
HCHO	-47.3	-46.8	-40.0	-3.6	-36.5
CH ₃ CH ₂ OH	-55.0	-57.9	-47.0	-4.2	-42.9
CH ₃ OH ^[a]	-48.1	-51.7	-40.0	-4.5	-35.6
HCl	-39.2	-39.4	-37.1	-4.8	-32.2
CHCl ₃	-50.3	-46.8	-43.6	-5.2	-38.4
CH ₂ F ₂	-52.3	-54.9	-45.4	-5.8	-39.6
H ₂ O ^[a]	-50.7	-55.1	-42.3	-6.8	-35.4
Benzene	-41.6	-38.9	-35.2	-7.4	-27.8
HF	-45.7	-53.2	-38.4	-8.0	-30.4
CH ₃ CN ^[a]	-59.2	-63.2	-52.1	-11.7	-40.5
CH ₂ Cl ₂ ^[a]	-60.0	-61.3	-53.0	-12.0	-41.0
Aniline ^[a]	-69.8	-71.0	-61.9	-15.3	-46.6
Dimethylsulfone ^[a]	-70.2	-77.3	-62.2	-16.2	-46.0
HCOOH ^[a]	-70.5	-90.8	-62.0	-16.9	-45.1
Phenol	-70.0	-73.1	-62.0	-17.0	-45.0
Benzoic acid	-72.6	-75.9	-68.2	-17.1	-51.1
CH ₃ NO ₂ ^[a]	-69.6	-74.1	-59.5	-20.0	-39.4
HCN	-56.2	-53.8	-50.6	-21.2	-29.4
HCONH ₂ ^[a]	-77.8	-82.4	-69.0	-21.3	-47.7
Methanesulfonamide ^[a]	-89.1	-95.1	-81.6	-32.6	-49.0
NH ₂ CN ^[a]	-88.4	-98.0	-80.2	-34.5	-45.7
CH ₂ (NO ₂) ₂	-103.0	-113.5	-93.8	-36.2	-57.6
Malononitrile ^[a]	-97.4	-102.4	-89.1	-40.1	-49.0

[a] Observed; corresponds to a known crystal structure.

The G4(MP2) interaction energy (ΔE) for 18C6 complexes (Table 1) was computed from the electronic energy of the complex (dimer) minus the sum of those for the isolated monomers, using the optimised geometries for each moiety: $\Delta E = E(\text{complex}) - E(18\text{C6}) - E(\text{guest})$.[‡] Enthalpies (ΔH), entropies (ΔS) and Gibbs free energies (ΔG) at 298 K are also reported in the table. The G4(MP2) composite method has been shown to produce gas-phase thermochemical properties such as reaction energies and enthalpies of formation with a mean absolute deviation (MAD) of 4.4 kJ mol⁻¹ from the experimental energies of the G3/05 test set.^{19, 29} Table 1 also reports interaction energies determined with the CE-B3LYP model, using the same optimised geometries determined for each monomer in the respective complex. This model has been shown to reproduce benchmark DFT interaction energies with a MAD of just over 1 kJ mol⁻¹, but in considerably less

Fig. 1. G4(MP2) free energies of complex formation at 298 K versus G4(MP2) complexation energies. Filled red circles denote 18C6:guest complexes that have been observed experimentally.

computation time.²⁰ It also performs surprisingly well (MAD of 2.5 kJ mol⁻¹) for a combined data set of CCSD(T)/CBS benchmark energies for 152 molecular dimers from the literature. The major advantage of the CE-B3LYP model is that the calculations are considerably more efficient, but provide reliable interaction energies which do not deviate far from the advanced hybrid and composite method results. An additional rationale for their inclusion here is for further validation of the CE-B3LYP approach for intermolecular interaction energies. For this purpose, we compare $\Delta E(\text{CE-B3LYP})$ with $\Delta E(\text{G4(MP2)})$, and explore to what extent the computation of ΔE can be used to estimate a quantity like $\Delta G_{298\text{K}}$.

Fig. 1 plots $\Delta G_{298\text{K}}$ against $\Delta E(\text{G4(MP2)})$, and it is clear that the two quantities are correlated; $R^2 = 0.872$, and a trend line through the data yields the expression $\Delta G_{298\text{K}} = 0.703 \Delta E(\text{G4(MP2)}) + 31.4$ (in kJ mol⁻¹), providing estimates of $\Delta G_{298\text{K}}$ with a MAD of just 4 kJ mol⁻¹. Importantly, Fig. 1 highlights

Fig. 2. Optimised geometries for 1:1 18C6 complexes with CO₂ and CS₂. In this and subsequent figures the host molecule is shown in the same orientation as far as possible. Hydrogen bonds are indicated by green dashed lines and other close contacts by magenta dashed lines.

those dimer motifs that have been observed in 18C6 host:guest crystal formation. A detailed discussion of these crystal structures, in particular a comparison between observed and optimised geometries, is provided in the following section. Here we focus on thermodynamic aspects and explore whether the present $\Delta G_{298\text{K}}$ values for 18C6:guest dimer formation in the gas phase can provide insight into the formation (or otherwise) of the respective crystalline complexes, and in particular the commonly observed centrosymmetric 18C6:(guest)₂ motif.

The observed motifs all have significantly negative values of $\Delta G_{298\text{K}}$, with the exception of acetic acid and ammonia ($\Delta G_{298\text{K}} = -0.1$ and $+5.5$ kJ mol⁻¹, respectively). The observation of the 18C6:(ammonia)₂ binary complex is readily understood because in both instances where the complex has been isolated and characterized it was prepared at ~100 K below room temperature,^{12, 30} which reduces the magnitude of $T\Delta S$ by ~13 kJ mol⁻¹ and shifts the free energy of complexation from $+5.5$ kJ mol⁻¹ at 298 K to -7.5 kJ mol⁻¹ at ~200 K. The 18C6:(acetic acid)₂ crystalline complex reported by Albert and Mootz³¹ incorporates two *syn* monomers in an acetic acid dimer, which in turn links two 18C6 molecules through weaker and non-directional $-\text{CH}_3\cdots\text{O}$ interactions (i.e., the relatively electropositive methyl groups sit above the electronegative centre of the crown molecule). The optimised geometry for the 1:1 18C6:(acetic acid) complex in the present work is somewhat different, as the acetic acid conformation is *anti*, with a single C-O-H $\cdots$ O hydrogen bond to one of the crown oxygens in addition to the weaker $-\text{CH}_3\cdots\text{O}$ interactions. The preference for acetic acid to dimerize in the crystalline binary complex can be understood by observing that at the G4(MP2) level its binding energy is -66.2 kJ mol⁻¹ (which compares favourably with a mean of -61.9 ± 1.7 kJ mol⁻¹ from experiment³²) and $\Delta G_{298\text{K}} = -14.7$ kJ mol⁻¹, compared with ΔE and $\Delta G_{298\text{K}}$ values of -52.0 kJ mol⁻¹ and -0.1 kJ mol⁻¹, respectively, for complexation with the crown (Table 1). For this reason the computed free energy of formation for the present 18C6:(acetic acid) dimer cannot be used to draw firm conclusions about the formation of the crystalline complex.

Although there are no measurements of thermodynamic properties of 18C6 complexes with neutral guests in the gas phase, measurements have been reported for complexation with acetonitrile, nitromethane and malononitrile in C₆D₆,³³

and for malononitrile in CDCl_3 .³⁴ Binding enthalpies, $\Delta H_{298\text{K}}$, in C_6D_6 are -25.1 (acetonitrile), -31.8 (nitromethane) and -59.4 kJ mol^{-1} (malononitrile), a trend that is echoed by the present gas-phase values in Table 1 (-52.1 , -59.5 and -89.1 kJ mol^{-1} , respectively). The change of solvent to CDCl_3 lowers $\Delta H_{298\text{K}}$ for malononitrile to -22.2 kJ mol^{-1} . Measured free energies, $\Delta G_{298\text{K}}$, in C_6D_6 are $+2.3$ (acetonitrile), -0.6 (nitromethane) and -11.3 kJ mol^{-1} (malononitrile), while the value for malononitrile in CDCl_3 drops to -8.4 kJ mol^{-1} .

Predicted structures of 1:1 18C6:guest complexes

Fig. 3. Optimised geometries for 18C6 complexes with H_2O and H_2S .

From Fig. 1, strong candidates for 18C6 complex formation are obviously dinitromethane, phenol, HCN and benzoic acid, but the presence of a large number of data points clustered within 10 kJ mol^{-1} of $\Delta G_{298\text{K}} = 0$ in the plot suggests that many of those guest molecules may also form stable crystalline complexes with 18C6 under certain conditions (in particular lower temperature and choice of a suitable solvent). For this reason we discuss details of the predicted gas phase structures for some of these 1:1 complexes.

The complexes with CO_2 (D_{3d}) and CS_2 (C_s) are predicted to have similar complexation energies, but quite different geometries (Fig. 2). For CO_2 the guest is actually threaded in the crown, with carbon equidistant from the crown oxygen atoms (2.912 Å, much less than the sum of van der Waals radii), a geometry consistent with the sign of its quadrupole moment.³⁵ The crown shows almost no change from the D_{3d} structure for an isolated molecule (e.g., $\text{O}\cdots\text{O}$ distance across the ring in the isolated molecule optimised geometry is 5.818 Å). Although the predicted Gibbs free energy of complexation is zero at 298 K, it is possible that this structure may be

isolated and characterized, perhaps by crystallization from supercritical CO_2 . CS_2 has a quadrupole moment of opposite sign to that for CO_2 ,³⁵ and as a consequence the predicted geometry has one sulfur atom above the crown and the other relatively close to two of the crown hydrogen atoms. The free energy of formation of -3.0 kJ mol^{-1} suggests this complex is likely to be crystallized.

18C6 complexes with water and hydrogen sulfide (Fig. 3) are predicted to have similar C_s geometries, in both cases bridging the crown to form two hydrogen bonds, with $\text{H}\cdots\text{O}$ distances 2.102 and 2.234 Å, respectively. This bridging geometry has been observed in numerous crystalline hydrates

Fig. 5. Optimised geometries for 18C6 complexes with CF_4 and CCl_4 .

of 18C6^{36} (see below for further discussion). The $18\text{C6}:\text{H}_2\text{S}$ moiety has not been observed to our knowledge, but its predicted complexation free energy of $+1.2$ kJ mol^{-1} suggests it should be observable at low temperature.

Fig. 4 compares predicted geometries for the four linear molecules, HF and HCl (both C_s), and HCN (C_{3v}) and acetylene (D_{3d}). In all cases the electropositive hydrogen forms hydrogen bonds to one or more ring oxygen atoms. HF is unusual, forming a single very short hydrogen bond ($\text{F}\cdots\text{O}$ distance 1.606 Å) to one ring oxygen, and is arguably not 'complexed' by the crown. HCl forms a bridge across the ring with one short and two longer hydrogen bonds ($\text{Cl}\cdots\text{H}\cdots\text{O}$ distances 2.501 Å and 2.744 Å), while HCN and acetylene form symmetric complexes with three equal and long $\text{H}\cdots\text{O}$ hydrogen bonds ($\text{C}\cdots\text{H}\cdots\text{O}$ distances of 2.860 Å and 2.935 Å, respectively). None of these motifs has been observed, but all are predicted to have negative complexation free energies at 298 K.

Structures of 18C6 with CF_4 and CCl_4 (Fig. 5) are predicted to be similar, with one halogen atom sitting above the ring. For $18\text{C6}:\text{CF}_4$ the bound halogen lies at the centre of the ring, resulting in a structure with C_{3v} symmetry (the $\text{F}\cdots\text{O}$ distances are 2.980 Å). In contrast, for $18\text{C6}:\text{CCl}_4$ the bound Cl atom lies off-centre, with three different $\text{Cl}\cdots\text{O}$ distances (one short at 3.058 Å, others at 3.435 and 3.468 Å). CCl_4 is predicted to be more strongly bound, with a small negative free energy of complexation, and hence likely to be observable. CF_4 , on the other hand, is one of the most weakly bound systems in the present study (see Fig. 1), and unlikely to be observed.

Structures of the 18C6 complexes with disubstituted methanes (Fig. 6) show a number of similarities. All have C_s symmetry, with the methylene hydrogen atoms situated asymmetrically above the ring; the shortest methylene- $\text{H}\cdots\text{O}$ distances are all considerably shorter than the respective sum

Fig. 4. Optimised geometries for 18C6 complexes with linear molecules HF, HCl, HCN and HCCH.

of van der Waals radii (2.306 Å (F), 2.181 Å (Cl), 2.136 Å (CN))

Fig. 6. Optimised geometries for 18C6 complexes with difluoromethane, dichloromethane, malononitrile and dinitromethane.

and 2.207 Å (NO₂)). There is also clear evidence of interactions between terminal atoms F, Cl, N and O with hydrogen atoms of the ring, in particular for dinitromethane, where the nitro O atoms show N...H separations of 2.544, 2.519 and 2.509 Å. Complexation energies for this family of guests are all substantial, those for malononitrile and dinitromethane being the greatest in the present study. Free energies are negative for this family, in agreement with the observation of the 18C6:(guest)₂ motif in crystals with dichloromethane¹¹ and malononitrile,⁸ and indicating that the complexes with difluoromethane and dinitromethane should also be observable.

Comparison between CE-B3LYP and G4(MP2) complexation energies

A cursory inspection of Table 1 reveals a strong correlation between $\Delta E(\text{CE-B3LYP})$ and $\Delta E(\text{G4(MP2)})$, and this is borne out in Fig. 7(a), where the MAD is 4.8 kJ mol⁻¹. However, the figure also identifies conspicuous outliers of two kinds: (i) where $\Delta E(\text{G4(MP2)})$ is much greater than $\Delta E(\text{CE-B3LYP})$ (i.e., formic acid, acetic acid, cyanamide and dinitromethane); and (ii) where the opposite is true (CS₂ and CCl₄). The first category results from ignoring the energy associated with geometric rearrangement that occurs between the monomers in isolation, and in the 1:1 18C6:guest complex. In other words, the G4(MP2) energy difference refers to optimised geometries of isolated monomers and their respective (and different) geometries in the complex, while the CE-B3LYP energy is computed using only the geometries of monomers in the complex. This rearrangement energy is by definition positive, and can be quite substantial (Table S1 of the ESI). The largest G4(MP2) rearrangement energy for 18C6 occurs in its

complexes with malononitrile and phenol (5.9 kJ mol⁻¹) and dinitromethane (5.3 kJ mol⁻¹). Much greater rearrangement

Fig. 7. Comparison between CE-B3LYP and G4(MP2) complexation energies, (a) before, and (b) after correction for the G4(MP2) rearrangement energy. The straight line has unit slope.

energies occur for three guest molecules: acetic acid (23.7 kJ mol⁻¹), formic acid (19.0 kJ mol⁻¹) and dinitromethane (11.1 kJ mol⁻¹). Correcting the G4(MP2) energies in this way reduces the MAD from CE-B3LYP energies to only 3.4 kJ mol⁻¹, although it is clear that the original discrepancy for CS₂ and CCl₄ still remains (Fig. 7(b)). The reason for this is less clear. We have confirmed that the CE-B3LYP model energies closely approximate the actual B3LYP-D2/6-31G(d,p) counterpoise corrected energies upon which the model is based²⁰ (they agree to within 1.5 kJ mol⁻¹ for both complexes). But it is noteworthy that these are the only two complexes of those under consideration where a heavy atom lies in close proximity to the oxygen atoms of the crown. For 18C6:CCl₄ the

shortest Cl...O distance is 3.058 Å (~0.21 Å less than the sum of vdW radii), and for 18C6:CS₂ there are close contacts of 3.102 and 3.098 Å (~0.22 Å less than the sum of vdW radii). This suggests a cause related to the proximity of S or Cl to oxygen, and we tentatively ascribe this to the lack of a correction for basis set superposition error (BSSE) in the G4(MP2) methodology.

Decomposition of the CE-B3LYP complexation energies

One important advantage of the CE-B3LYP model for interaction energies is its decomposition into four components, and in particular an estimate of the separation between electrostatic, polarization and dispersion contributions to the binding of these complexes (Table S2 of the ESI). Fig. 8 plots the CE-B3LYP dispersion energy against the sum of electrostatic and polarization energies (i.e., an estimate of the total classical electrostatic contribution). In all cases the values are those scaled quantities that comprise the total CE-B3LYP interaction energy.²⁰ We see from the figure that the vertical line at $E_{\text{ele}} + E_{\text{pol}} = -50 \text{ kJ mol}^{-1}$ marks an approximate boundary between observed and (as yet) unobserved motifs, as well as all 1:1 complexes for which $\Delta G_{298\text{K}}$ is positive. To the left of this boundary lie several 1:1 18C6:guest complexes where $\Delta G_{298\text{K}}$ is negative, and which are definite candidates for future study. Equally, the figure identifies a large number of 1:1 complexes worthy of further study, for which $\Delta G_{298\text{K}}$ is negative but $E_{\text{ele}} + E_{\text{pol}}$ is much smaller.

Comparison of predicted 1:1 18C6:guest structures with those observed in crystals

The focus of discussion so far has been on computational predictions of the structures and geometries of 1:1 complexes in the gas phase, and their relevance to the observation (or otherwise) of such a motif in crystal structures of 18C6 with neutral molecules. An important consideration that also needs to be addressed is how well these predicted geometries for simple dimers in isolation correspond with observed crystal structures. Here we provide a detailed comparison between all of those motifs identified above as “observed” (Figs. 1 and 8, and Table 1) and known crystal structures. Fig. 9 displays the results of overlaying 1:1 predicted structures with corresponding molecular pairs extracted from known crystal structures for all of these “observed” motifs, with the exception of aniline.⁵ Fig. 9 convincingly demonstrates that there is overall excellent agreement between predicted structures of 1:1 gas phase complexes and their crystalline counterparts. CE-B3LYP model energies for experimental structures (with X–H bond lengths normalised as usual) are used to explore the ramifications of differences between predicted and observed guest orientations.

Ammonia

The crystal structure of the 18C6:(ammonia)₂ complex has been independently reported by Nuss and Jansen¹² (CSD refcode KATLAT) and Suchentrunk *et al.*³⁰ (KATLAT01). The predicted and observed structures are very close, with three

identifiable N–H...O hydrogen bonds. The only significant difference is the distance of the guest molecule N atom above

Fig. 8. Scatter plot of electrostatic vs dispersion components of the CE-B3LYP model energies for 1:1 18C6:guest complexes. Data points highlighted with a red cross identify 18C6:(guest)₂ complexes that have been observed.

the mean plane of the ring oxygens: 1.70 Å predicted vs 1.85 Å (KATLAT) and 1.88 Å (KATLAT01).

Acetic acid

Albert and Mootz reported crystal structures of the 18C6:(acetic acid)₂ complex (NURHOX) as well as a stoichiometric hydrate, 18C6:(acetic acid)(H₂O) (NURHUD).³¹ As noted earlier, in the 1:2 complex the acetic acid molecules dimerize and as a consequence they have a *syn* conformation, rather than the *anti* conformation predicted for the 1:1 structure, and this difference is reflected in the different guest orientations in Fig. 9. In the monohydrate structure *syn* acetic acid molecules display a similar interaction with 18C6, with methyl groups above one 18C6 ring, and also form a C–H...O hydrogen bond to a water molecule, which in turn forms a bridge across O1 and O7 atoms in the crown (see further details for water structures below). A further dimorphic ternary phase was also reported by Albert and Mootz, 18C6:(acetic acid)₂(H₂O)₄, where only the water molecules are bound to the crown (NURJEP, NURJEP01).

Methanol

To our knowledge there are no known crystal structures of the 18C6:(methanol)₂ complex by itself, but it has been observed in methanol solvates of 18C6 with bis(benzenesulfonyl)amine (YINFEG) and its bis(4-chlorobenzenesulfonyl) analogue (YINFIK); the 1:1 18C6:methanol motif also occurs with benzenesulfonyl-methylsulfonylamine (YINFUW).³⁷ There is close similarity between the predicted 1:1 structure and the observed moiety in Fig. 9, both showing a single hydrogen

bond between the methanol OH and a ring oxygen, with the methyl group bridging two other ring oxygen atoms. The predicted hydrogen bond O...O distance is 2.86 Å, compared with observed values of 2.84 Å (YINFEG), 2.69 Å (YINFIK) and 2.76 Å (YINFUW).

Water

The crystal structures of four stoichiometric hydrates of 18C6 are known: 18C6:(H₂O)₄ (REGRAW^{36b} and REGRAW01³⁸), 18C6:(H₂O)₆ (YIMZAV^{36a} and YIMZAV01³⁸), 18C6:(H₂O)₈ (REGREA^{36b}) and 18C6:(H₂O)₁₂ (REGRIE^{36b}). In all of these structures one water molecule forms a bridge across the ring, with hydrogen bonds to O1 and O7 of the ring, and this interaction has been shown computationally to be the most stable for a monohydrate of 18C6.¹⁷ The centrosymmetric 18C6:(H₂O)₂ motif with these bridging water molecules can also be found in a large number of other crystal structures in the CSD. The predicted geometry of the present 1:1 complex is clearly very close to that observed in the tetrahydrate (Fig. 9); the predicted O1—O_{water}—O7 angle is 108° compared with 110° (REGRAW; REGRAW01) 108° and 107° (YIMZAV; YIMZAV01), 109° (REGREA) and 110° (REGRIE).

Acetonitrile

The complex of 18C6 with acetonitrile was one of the first 18C6:neutral guest complexes to be identified, originally in the context of purification of 18C6 by removal of acetonitrile from the complex under vacuum.³⁹ It was subsequently characterised by Knöchel and co-workers⁴⁰ who reported a stoichiometry of 1:1.6. The crystalline 1:2 complex contains the 18C6:(acetonitrile)₂ centrosymmetric moiety, and is dimorphic. The low-temperature *P* $\bar{1}$ form has two 18C6:(acetonitrile)₂ moieties (GEFREO^{10a}), whereas the form observed at room temperature has only one (GEFREO01^{10b} and GEFREO02⁴¹). The thermal expansion of 18C6:(acetonitrile)₂ has also been very recently studied over the range 180 to 273 K.⁴² The predicted structure agrees well with experiment, with two of the methyl H atoms directed into the crown cavity, and the cyano group tilted towards two of the H atoms of the crown. In the predicted structure the C-C-N vector lies closer to the crown than observed in the solid state, making an angle of 40° with the mean plane of ring oxygens, compared with 57° (GEFREO01; GEFREO02) and 49° and 59° (GEFREO). This tilting away from the crown can be understood by the attractive antiparallel dipole-dipole interaction that occurs between acetonitrile molecules bound to adjacent crowns in all of these crystal structures, and for which the energy estimates are -18 kJ mol⁻¹ (GEFREO) and -14 kJ mol⁻¹ (GEFREO02).

It is also noteworthy that 18C6:(acetonitrile) complexes have also been observed in ternary co-crystals with two sulfonamides.⁴³ One incorporates the centrosymmetric 1:2 complex (HADMOO), but with the acetonitrile also hydrogen bonded to the amide and as a result almost perpendicular to the crown; the other incorporates the 1:1 complex (HADMUU) with a similar geometry to that predicted here.

Dichloromethane

The crystal structure of the 1:2 centrosymmetric 18C6:(dichloromethane)₂ complex (YEGVIP¹¹) was determined by Jones *et al.* from crystals “fortuitously grown from a dichloromethane solution containing 18-crown-6 and sulfur trioxide”. The observed and predicted geometries are in excellent agreement (Fig. 9), with the electropositive methylene H atoms bridging O1 and O10 atoms of the ring. The predicted structure has C_s symmetry (not C_{2v}, which might have been expected), with an asymmetric bridge incorporating C...O distances of 3.62 Å and 3.26 Å (Fig. 6), compared with 3.66 Å and 3.35 Å in the crystal. The energy difference between observed and predicted structures is only 1.9 kJ mol⁻¹. Guest:guest dipole:dipole interactions in the crystal are less than 2 kJ mol⁻¹.

Formamide

The 1:2 18C6:(formamide)₂ complex was isolated by Vögtle *et al.* in 1980,⁴⁴ and its crystal structure reported a few years later (CEHGEB⁴⁵). The predicted geometry for the 1:1 dimer (Fig. 9) is in excellent agreement with the observed structure, with both amine hydrogen atoms forming hydrogen bonds to O1 and O7 ring oxygens (predicted N...O distances are 2.99 Å and 3.08 Å, compared with 3.00 Å and 3.04 Å in the crystal). The CE-B3LYP interaction energy for this geometry is -80.6 kJ mol⁻¹, only slightly smaller than that obtained for the predicted geometry (-82.4 kJ mol⁻¹, Table 1). The angle between the formamide plane and the mean plane of ring oxygens differs by only 4° between predicted and observed geometries, indicating that the centrosymmetric C-H...O interaction between guest molecules in the crystal (estimated binding energy of -20 kJ mol⁻¹) causes only a minor perturbation.

Dimethylsulfone

The overlay of the predicted 1:1 and observed 1:2 (CRMESF⁴⁶) structures for the 18C6:dimethylsulfone complex (Fig. 9) suggests significant differences, but the essential binding element is the same in both cases, namely several C-H...O contacts with ring oxygens from one of the guest's methyl groups. The orientation of the C-S bond differs, once more due to intermolecular interactions between guest molecules in the crystal, which form a strongly bound cyclic dimer (estimated binding energy of -40 kJ mol⁻¹) that in turn links two adjacent crowns. The observed 1:1 complex geometry in the crystals is estimated to lie approximately 11 kJ mol⁻¹ above that predicted by theory.

Formic acid

From Fig. 9 the predicted and observed (NURHIR³¹) 1:1 structures of 18C6:formamide are in very close agreement. The guest molecule has the *E* form, and lies roughly perpendicular to the ring, making a O-H...O hydrogen bond to a ring oxygen (predicted O...O distance of 2.78 Å, compared with 2.69 Å observed). Unlike acetic acid and dimethylsulfone, the formic acid guest molecule interacts only with other crown molecules in the crystal. The observed geometry lies less than 1 kJ mol⁻¹ above that predicted by theory.

Fig. 9. Overlay of predicted structures for 1:1 18C6:guest complexes (in full colour for all atoms) and the corresponding pair of molecules extracted from an observed crystal structure (identified by a CSD refcode; the 18C6 host is blue and the guests magenta in all cases). The superposition has been performed with Mercury,¹ minimising the sum of distances between the six crown oxygen atoms of predicted and observed 18C6 molecules. The orientation of the 18C6 molecule is the same in all cases, and ring oxygen atoms pointing upwards are indicated with a + symbol for the ammonia complex

Nitromethane

The 1:2 18C6:(nitromethane)₂ complex is the most studied complex of 18C6 with a neutral guest. It was first characterised by Knöchel and co-workers⁴⁰ who reported a stoichiometry of 1:1.8, and its crystal structure has been determined at room temperature by de Boer *et al.* (BIJWAS³³), at room temperature (BIJWAS01⁴⁷) and 123 K (BIJWAS02⁴⁸) by Rogers *et al.*, and most recently its thermal expansion was studied over the range 180 to 273 K by Barbour and co-workers (BIJWAS03 to BIJWAS10^{42,49}). The interaction with the crown is similar to others with a methyl group attached to electron withdrawing atoms, and from Fig. 9 the only significant difference between predicted and observed structures is the orientation of the nitro group. The energy estimate for the observed 1:1 complex in BIJWAS03 is -68 kJ mol⁻¹, 6 kJ mol⁻¹ above that for the predicted geometry. An attractive guest:guest dipole:dipole interaction occurs in the crystal with a binding energy of -16 kJ mol⁻¹, a very similar result to that for acetonitrile.

Methanesulfonamide

The crystal structure of the 1:2 18C6:(methanesulfonamide)₂ complex was reported in earlier work by some of us (YUSRAH¹³), and the situation here follows much the same pattern as seen for dimethylsulfone. The overlaid structures in Fig. 9 appear quite different, but the only real difference is in the angle made with the crown ether plane, resulting from a relatively strong interaction between guest molecules, which form a cyclic dimer (energy -27 kJ mol⁻¹) linking two adjacent crown hosts. The observed structure lies only 3 kJ mol⁻¹ above that reported in Table 1.

Cyanamide

The 1:2 18C6:(cyanamide)₂ complex was first characterised by Knöchel and co-workers who reported a stoichiometry of 1:2 and determined its crystal structure at room temperature (CENHAE⁷). Subsequent X-ray (CENHAE01) and neutron (CENHAE02) crystal structures were determined at 100 K in an experimental charge density study by Koritsanszky *et al.*⁵⁰ The predicted and observed structures are clearly close, and as noted for acetonitrile the difference between the two arises

from an attractive guest:guest dipole:dipole interaction in the crystal (-14 kJ/mol). The observed structure lies only 4 kJ mol⁻¹ above that reported in Table 1.

Malononitrile

The 18C6 complex with malononitrile was also first characterised by Knöchel and co-workers⁴⁰ and its crystal structure at room temperature was reported a year later (HODMLN⁸). Its binding mode to the crown is the same as that for dichloromethane, but with a more asymmetric bridge (Fig. 6, C...O distances of 3.87 Å and 3.15 Å, compared with 3.57 Å and 3.26 Å in the crystal). The energy difference between observed and predicted structures is 5 kJ mol⁻¹ and the guest:guest dipole:dipole interaction in the crystal amounts to -23 kJ mol⁻¹.

Conclusions

This work presents the first detailed computational study at a very high level of theory focused on complexation of 18C6 with neutral molecules. G4(MP2) theory has been used to determine binding energies and subsequent thermodynamic properties at 298 K for complexation of 1:1 neutral 18C6:guest complexes in the gas phase. These properties correlate exceptionally well with the observed/unobserved status of relevant 1:1 and 1:2 complexes in the crystalline state, and comparison between predicted geometries of 1:1 complexes and those observed in crystals demonstrates excellent agreement. Differences between the two can be clearly attributed to the presence of relatively strong interactions between guest molecules. The fact that the predicted geometries of 1:1 complexes from gas phase optimizations match strikingly well with the observed crystal geometries identifies the 18C6:guest and 18C6(guest)₂ motifs as important modular units in supramolecular recognition, units which are relatively unperturbed by their interactions with the rest of the crystalline environment.

CE-B3LYP model interaction energies for these 1:1 complexes agree well with G4(MP2) values (MAD of 3.4 kJ mol⁻¹), provided corrections are made to the latter for the energy associated with rearrangement of monomer geometries. These rearrangement energies are relatively small for the crown host (less than 6 kJ/mol), but can be quite substantial for some guests, and in particular acetic and formic acid where they reflect the respective *syn/anti* and *E/Z* energy differences. CE-B3LYP energies were also shown to provide valuable insight into the often small energy differences that result from minor changes in position and orientation of guest molecules between predicted and observed structures. Perhaps the most important prediction emerging from this work is the identification of the large number of other 18C6 complexes with neutral guests that are likely to be observed, especially with careful choice of preparation conditions.

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Notes and references

‡ The reference structure for 18C6 in the gas phase has D_{3d} symmetry. Although there are many gas phase geometries for 18C6 with similar energies, the differences depend greatly on the level of theory and basis set used.⁵¹ In addition, the geometry of 18C6 is also solvent-dependent.⁵² For simplicity, and because it does not make a substantive difference which we use, we have chosen the D_{3d} geometry.

§ The crystalline 18C6:(aniline)₂ complex was reported by Elbasyouny et al.,⁷ among a number of complexes between 18C6 and neutral guests with NH acidic groups, but no crystal structure has been reported, and that work indicated that the aniline complex also contained a nonstoichiometric amount of water.

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